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DEPENDENCE OF THE VISCOSITY OF BASALT MELTS ON THE CHEMICAL COMPOSITION OF THE INITIAL MINERAL MATERIAL

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An approximate relation for calculating the viscosity of fused basaltic glass according to the chemical composition of the initial mineral raw material is proposed. This relation was obtained as a result of a multifactor regression analysis of a set including 27 rocks. The experimental values of the viscosity of melts and x-ray fluorescence data on the content of oxides in the raw material were used in the modeling. The relation makes it possible to predict to a high degree of accuracy the viscosity of melts at a prescribed temperature.

Key words: rocks, mineral raw material, chemical composition, acidity modulus, melt, viscosity, regression analysis.

One of the most important physical-chemical properties of aluminosilicate glass that determine the suitability of the glass for manufacturing different types of fibers is the viscosity η , which is usually compared with the values of the acid-base indicators, first and foremost, the acidity modulus M_a calculated as the ratio of the mass content (%) of four melt-forming oxides:

$$M_a = \frac{\text{SiO}_2 + \text{Al}_2\text{O}_3}{\text{CaO} + \text{MgO}}.$$

The larger the value of M_a of the initial raw material, the higher the viscosity of its melt is.

However, the magmatic rocks which are widely used in fiber manufacture are more complicated multicomponent systems which include at least nine oxides, each of which can affect the viscosity to some extent. In addition, as numerous experimental studies of raw materials from different deposits have shown, the effect of any particular oxide on the melt viscosity is determined not only by its nature but also by its content. Silica SiO_2 , alumina Al_2O_3 , magnesium oxide MgO , and trivalent iron Fe_2O_3 are viscosity-increasing oxides. Alkali metal oxides K_2O and Na_2O and divalent iron FeO lower the viscosity; the effect of others, including CaO , is quite complex and not unique: up to certain content they decrease the viscosity and above this value the viscosity of the melt increases or vice versa.

Repeated attempts to predict the viscosity of melts from the chemical composition of the rocks have been made. Using of mathematical modeling the authors of [1] obtained for two sets of raw materials with different chemical composition regression equations relating the values of the logarithm of the viscosity at temperature 1400°C with the content of the main oxides in the rock:

$$\begin{aligned} \log \eta_{1400^\circ\text{C}} = & 0.658 + 0.003\text{SiO}_2 - 0.0057\text{TiO}_2 + \\ & 0.0025\text{Al}_2\text{O}_3 - 0.0078\text{Fe}_2\text{O}_3 - 0.0039\text{FeO} + \\ & 0.0028\text{MgO} - 0.0027\text{CaO} - \\ & 0.0003\text{Na}_2\text{O} + 0.0036\text{K}_2\text{O}; \end{aligned} \quad (1)$$

$$\begin{aligned} \log \eta_{1400^\circ\text{C}} = & 1.613 + 0.0023\text{SiO}_2 - 0.0038\text{TiO}_2 + \\ & 0.0023\text{Al}_2\text{O}_3 - 0.0094\text{Fe}_2\text{O}_3 - \\ & 0.0046\text{FeO} + 0.0031\text{MgO} - \\ & 0.0036\text{CaO} - 0.0014\text{Na}_2\text{O} + 0.00226\text{K}_2\text{O}; \end{aligned} \quad (2)$$

where SiO_2 , TiO_2 , and others denote the oxide content, molar fraction $\times 10^3$.

The equation (1) was derived for rock melts for which $\log \eta$ varies from 0.5 to 3.6, while in the second equation this quantity is in the range 1.4 – 2.5. The coefficients of the factors in the equations are different; correspondingly, the viscosity values obtained from Eq. (1) and (2) are also different. In addition, for the chosen composition the individual oxides MgO and K_2O increase the viscosity according to the first equation and decrease it according to the second equation.

Similar relations have also been obtained for other sets of raw materials at different temperatures. In addition, the computational accuracy for $\log \eta$ at 1450 and 1250°C is much

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lower than at 1300 and 1350°C, while the change in the coefficients in these equations from one temperature to another has no logical explanation. On this basis the equations presented cannot be regarded as correct and the viscosity values calculated using them as sufficiently accurate predictions of its real values.

The author of [2] proposed a relation, which includes the acidity modulus M_a , that he derived from experimental results obtained for batch melts with different Al_2O_3 , MgO , and CaO contents:

$$\log \eta = 0.785M_a - 0.00356t + 5.11.$$

Here $M_a = (\text{SiO}_2 + 2\text{Al}_2\text{O}_3)/(\text{2Fe}_2\text{O}_3 + \text{FeO} + \text{CaO} + \text{MgO} + 2\text{Na}_2\text{O} + 2\text{K}_2\text{O} + \text{MnO} + \text{TiO}_2 + \dots)$, and t is the temperature, °C.

The viscosity values computed at different temperatures and presented in [2] are largely at variance with the experimental data: the relative error fluctuates from 1.5 to 65%.

A structural–thermophysical theory has been developed for magmatic melts [3]. According to this theory the viscosity of melts can be calculated at their liquidus temperature without using the Frenkel–Andrade model theory of the viscosity [4]. The authors proposed using the thermophysical Fourier (Fo) and Biot (Bi) numbers and the Tikhonov number (Ti) to evaluate the temperature dependence of the viscosity [5]. Assuming the thermal diffusivity and heat emission for magmatic melts to be close to one another, they obtained the Einstein relation for the diffusion law in a different form [6] that made it possible to calculate the temperature variation of the melt viscosity as a function of the dimensionless numbers listed above:

$$\eta = \frac{RT}{6\pi A \text{ Bi Fo } \sqrt{\text{Fo}}} = \frac{RT}{6\pi A \text{ Ti Fo}},$$

where η is the viscosity, P; R is a constant; T is the temperature, K; A is the electronic polarization rate of non-bridge oxygen; and, Ti is the Tikhonov number (the homochronicity number for semi-infinite bodies).

A nomogram representing the relation between the degree of polarization of non-bridge oxygen in melt and the Tikhonov number is used to calculate the numbers Bi and Ti for different values of the Fourier number [7].

Making definite suppositions and assumptions about the degree of polarization of non-bridge oxygen and the degree of depolymerization of the melt, the authors of [3] propose the following equation for calculating the viscosity at the liquidus temperature:

$$\log \eta = \log \frac{RT}{6\pi^4 \text{ Bi Fo } \sqrt{\text{Fo}}}.$$

The viscosity values obtained with this equation likewise agree poorly with the experimental data.

Another method with a similar drawback for calculating the viscosity of magmatic melts from the chemical composition of the rock is Persikov's semi-empirical method [8]:

$$\log \eta = \log \frac{(a - bK) \times 10^3}{4.576T - 3.5 + \alpha(p_{\text{tot}} - p_{\text{H}_2\text{O}})},$$

where η is the viscosity, P; a and b are empirical regression coefficients; K is a structural-chemical parameter reflecting the ratio of the bridge O^0 and non-bridge O^- oxygen:

$$K = \frac{\text{O}^-}{\text{O}^0} = \frac{2(\text{O} - 2\text{M})}{\text{M}} \times 100;$$

O and M are the total numbers of gram-ions of oxygen and network-formers (Si^{4+} , Al^{3+} , Fe^{+3} , P^{5+}) in the melt, respectively; T is the temperature, K; p is the pressure, MPa; α is the piezo-viscosity coefficient, MPa^{-1} ; and, $\alpha = -5.02 \times 10^{-4} \text{ MPa}^{-1}$ for “dry” melts and $\alpha = -1.2 \times 10^{-3} \text{ MPa}^{-1}$ for incompletely water-saturated melts.

It should be noted that for calculations the author uses the concentrations of only three melt-forming oxides (SiO_2 , Al_2O_3 , Fe_2O_3), while their relative effects on the viscosity are neglected.

In summary, no computational method studied above gives reliable values for the viscosity of fused glass and the methods are quite complicated to use in production practice. In this connection, using a multifactor regression analysis program the present authors attempted to obtain the best fit representing the dependence of the viscosity of melts on the chemical composition of the raw material. An array of experimental data on the viscosity of basaltic melts of rocks from 27 deposits with different chemical composition in the temperature range 1200 – 1450°C was used for modeling.

The chemical composition of the rocks was determined by x-ray fluorescence using an SRM-25 computer-controlled multichannel x-ray spectrometer. Sample preparation was based on melting rock with active flux. State standard samples of natural rocks were used to check the validity of the analysis. The determination errors of the concentrations of different oxides in the control rocks with confidence probability 0.95 are presented in Table 1. The data are presented according to the OST 41-08212–82 second category of accuracy.

The viscosity at temperatures from 1200 to 1450°C was determined with a RVTS-K90R4 rotary viscosimeter. Its principle of operation reduces to measuring the time over which a coiled spring placed between a drive shaft and an inner cylinder, deforming the melt located between a stationary outer cylinder and the inner cylinder rotating with constant speed, turns through an angle. The absolute error of the measurement was $\pm 0.5 \text{ Pa} \cdot \text{sec}$.

The temperature t , acidity modulus M_a , and the mass content of oxides in basaltic rocks served as the initial parameters Z_i for obtaining an approximate relation.

TABLE 1. Determination Error for the Oxide Concentrations in the Control Rock

Oxide	Determination accuracy for standard samples	
	Content, wt. %	Absolute error, %
SiO ₂	60.60	±0.20
Al ₂ O ₃	18.20	±0.20
TiO ₂	0.95	±0.07
MnO	0.048	±0.005
Fe ₂ O ₃ + FeO	7.20	±0.15
MgO	2.20	±0.10
Na ₂ O	2.30	±0.10
K ₂ O	3.45	±0.15
P ₂ O ₅	0.18	±0.01
Other	4.70	±0.20

Note. Other — calcination losses.

A preliminary analysis with 12 parameters showed that SiO₂, Al₂O₃, CaO, and (FeO + Fe₂O₃) have the strongest effect on the melt viscosity. The effect of all other oxides is so weak as to be negligible.

Assuming that the indicated parameters interfere with one another weakly, the approximate relation has the generally accepted form

$$\eta = f(Z_1, Z_2, Z_3, Z_4, Z_5, Z_6) = a_0 Z_1^{a_1} Z_2^{a_2} Z_3^{a_3} Z_4^{a_4} Z_5^{a_5} Z_6^{a_6}, \quad (3)$$

where Z_1 is the SiO₂ content, wt.%, Z_2 the Al₂O₃ content, wt.%, Z_3 the CaO content, wt.%, Z_4 the (FeO + Fe₂O₃) content, wt.%; Z_5 is M_a ; and, Z_6 is the temperature, °C.

The problem was to find the seven unknown coefficients $a_0 \dots a_6$ in the relation (3).

The solution was obtained in two steps.

First, the least-squares method was used to find the coefficients to a first approximation ($\tilde{a}_0, \tilde{a}_1, \dots, \tilde{a}_6$), after which using direct-search technology the values were refined taking account of the relative effect of the parameters on the viscosity.

At the first step, denoting the experimental value of the viscosity of basaltic rocks as η_j ($j = 1, 2, \dots, 27$) and the viscosity values computed with the relation (3), into which the experimental data on the parameters Z_i ($i = 1, 2, \dots, 6$) are substituted, for the j th deposit as

$$\eta(a_0 Z_1^{a_1} Z_2^{a_2} Z_3^{a_3} Z_4^{a_4} Z_5^{a_5} Z_6^{a_6}) = \eta(Z_{ij}),$$

the squared differences between the experiment value η_j of the viscosity and the computed value $\eta(Z_{ij})$ were written as

$$F_j = [\eta_j - \eta(Z_{ij})]^2.$$

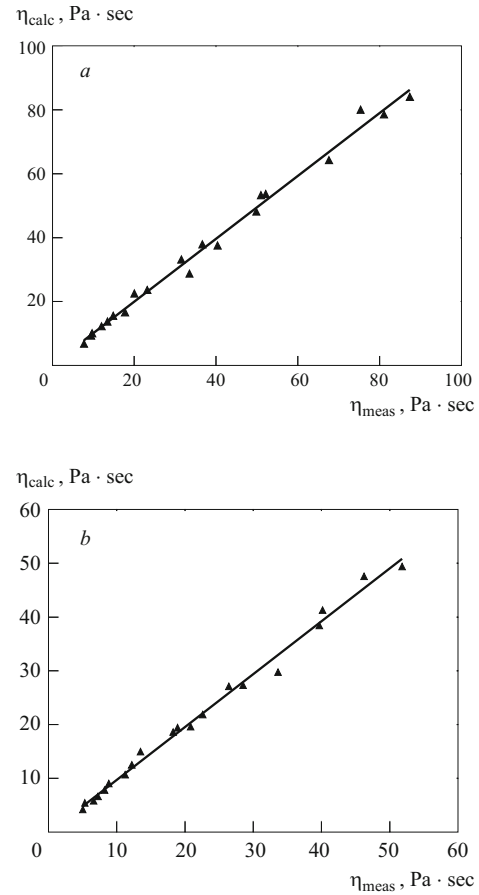


Fig. 1. Relation between the computed and measured values of the melt viscosity at temperatures 1350 (a) and 1400°C (b).

The sum of the squares of these differences is

$$F_{\Sigma} = \sum F_j = \sum_{j=1}^{27} [\eta_j - \eta(Z_{ij})]^2.$$

Next the minimum of the function F_{Σ} was found with respect to each parameter a_i . This gave the following system of seven equations with seven unknowns a_0, a_1, \dots, a_6 :

$$\left. \begin{aligned} \frac{dF_{\Sigma}}{da_0} &= 0 \\ \frac{dF_{\Sigma}}{da_1} &= 0 \\ &\dots\dots\dots \\ \frac{dF_{\Sigma}}{da_6} &= 0 \end{aligned} \right\}. \quad (4)$$

The coefficients \tilde{a}_i to a first approximation were determined by solving the system of equations (4) numerically.

At the second step refined values were found for the coefficients a_i using a computer program to perform a direct search.

For this we wrote down the equation

$$\tilde{\eta} = \tilde{a}_0 \tilde{Z}_1^{\tilde{a}_1} \tilde{Z}_2^{\tilde{a}_2} \tilde{Z}_3^{\tilde{a}_3} \tilde{Z}_4^{\tilde{a}_4} \tilde{Z}_5^{\tilde{a}_5} \tilde{Z}_6^{\tilde{a}_6}. \quad (5)$$

Each coefficient \tilde{a}_i was varied over the range $0.8\tilde{a}_i < a_i < 1.2\tilde{a}_i$ for all 27 rocks and the following minimum was found by the direct calculation using the relation (5):

$$\min |\eta_i - \eta(Z_i^{a_i})|.$$

The regression analysis established that there a real relation exists between the chemical composition of the rocks and the melt viscosity. This relation is described by a multifactor regression equation reflecting the individual and total M_a contribution of the melt-forming oxides:

$$\eta = 3.62(\text{SiO}_2)^{3.07}(\text{Al}_2\text{O}_3)^{-0.16}(\text{CaO})^{-0.40}(\text{FeO} + \text{Fe}_2\text{O}_3)^{1.34}(M_a)^{1.25}(t - 1100)^{-2.58}.$$

A positive sign of the exponent of oxide mass quantities signifies that for this set these exponents increase the viscosity; a negative sign signifies a decrease.

The equation obtained makes it possible to predict the melt viscosity to adequate accuracy at a prescribed temperature from the chemical composition of the raw material. This is confirmed by the data presented in Fig. 1 for rocks which were not included in the regression analysis.

It is especially important to use a computational method when using in fiber manufacture rocks whose melts reach the required viscosity at temperatures above 1450°C and technical difficulties appear in the experimental determination of the viscosity.

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